

Non-polarizing two-atom interaction potential in the liquid ^4He **D. B. Baranov**^a, **A. I. Kirillov**^b, **V. S. Yarunin**^{a, 1}^a *Joint Institute for Nuclear Research, Dubna 141980, Moscow Region, Russia*^b *Moscow Power Engineering Institute, Krasnokazarmennaja 14, E-250, Moscow 111250, Russia*

A formula for potential U of the ^4He – ^4He interaction in the liquid state is obtained by the direct electromagnetic computation as a function of the interatomic distance R . The potential decreases exponentially at large R . The further development and application of the result are discussed.

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It is known, that the Leonard–Jones (L–J) potential describes the interaction of atoms of simple non-polar gases [1]. However, at large distances between atoms the interaction forces fall faster, than it is described by the L–J potential [1]. The corresponding corrections (including light atoms) are suggested in papers [2]–[6]. These authors had a suspicion, that, for light atoms, either L–J formula or pair interaction approximation, or both of them are not valid. In this paper, we show that the rapid decrease of the potential can be explained, if we assume that the atom polarization is not important in the liquid.

In this paper, we calculate the potential U between charge densities of electrons and nuclei for ^4He in the ground state. The interaction energy of two charge distributions with the densities $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ is

$$U = \int \frac{\rho_1(\mathbf{r})\rho_2(\mathbf{r}')d\mathbf{r}d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}, \quad (1)$$

where the charge densities are

$$\begin{aligned} \rho_1(\mathbf{r}) &= q\delta(\mathbf{r} - \mathbf{r}_1) - q\mathbf{P}(\mathbf{r} - \mathbf{r}_1), \\ \rho_2(\mathbf{r}') &= q\delta(\mathbf{r}' - \mathbf{r}_2) - q\mathbf{P}(\mathbf{r}' - \mathbf{r}_2). \end{aligned} \quad (2)$$

Here $P(\mathbf{r} - \mathbf{r}_1)$ and $P(\mathbf{r}' - \mathbf{r}_2)$ are the electron probability densities at the points \mathbf{r} and \mathbf{r}' , the atom nuclei being at the points \mathbf{r}_1 and \mathbf{r}_2 , and $q = 2e$. Using (2) in (1), we have

$$\begin{aligned} \int \frac{\rho_1(\mathbf{r})\rho_2(\mathbf{r}')d\mathbf{r}d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} &= q^2 \int \frac{\delta(\mathbf{r} - \mathbf{r}_1)\delta(\mathbf{r}' - \mathbf{r}_2)d\mathbf{r}d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} - \\ &- q^2 \int \frac{\delta(\mathbf{r} - \mathbf{r}_1)\mathbf{P}(\mathbf{r}' - \mathbf{r}_2)d\mathbf{r}d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} - q^2 \int \frac{\delta(\mathbf{r}' - \mathbf{r}_2)\mathbf{P}(\mathbf{r} - \mathbf{r}_1)d\mathbf{r}d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} + \\ &+ q^2 \int \frac{P(\mathbf{r} - \mathbf{r}_1)P(\mathbf{r}' - \mathbf{r}_2)d\mathbf{r}d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} = U_{nn} + U_{nc} + U_{nc} + U_{cc} \end{aligned} \quad (3)$$

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It is evident, that the first term U_{nn} in (3) gives the interaction energy of two positive point-like charges of nuclei after the integration over coordinates \mathbf{r} and \mathbf{r}' :

$$U_{nn} = \frac{q^2}{R}.$$

The term U_{nc} describes the interaction between nucleus of an atom and electron cloud of another. We have

$$U_{nc} = -q^2 \int \frac{\delta(\mathbf{r} - \mathbf{r}_1) \mathbf{P}(\mathbf{r}' - \mathbf{r}_2) d\mathbf{r} d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} = -q^2 \int \frac{P(\mathbf{r}' - \mathbf{r}_2) d\mathbf{r}'}{|\mathbf{r}_1 - \mathbf{r}'|} = -q^2 \int \frac{P(\mathbf{r}_0) d\mathbf{r}_0}{|\mathbf{R} - \mathbf{r}_0|}, \quad (4)$$

where $\mathbf{r}_0 = \mathbf{r}' - \mathbf{r}_2$ and $\mathbf{R} = \mathbf{r}_1 - \mathbf{r}_2$. We assume that the electron probability density $P(\mathbf{r}_0)$ is spherically symmetric, the center being at the nucleus (the accuracy of this approximation is discussed at the end of the paper). Integration with respect to the spherical coordinates θ and φ in (4) gives

$$U_{nc}(R) = -\frac{q^2}{R} + 4\pi \frac{q^2}{R} \int_R^\infty P(r_0)(r_0^2 - Rr_0) dr_0 \quad (5)$$

We used the change of variable

$$\theta \rightarrow y = \sqrt{R^2 + r_0^2 - 2Rr_0 \sin \theta}, \quad \int_0^\pi \sin \theta d\theta \rightarrow \int_{|R-r_0|}^{R+r_0} \frac{y dy}{Rr_0}. \quad (6)$$

The cloud–cloud interaction term U_{cc} in (3) after the similar integration with respect to spherical coordinates becomes

$$U_{cc} = -\frac{2\pi}{R} \int_0^R U_{nc}(x) \int_{R-x}^{R+x} P(y) y dy x dx - \frac{2\pi}{R} \int_R^\infty U_{nc}(x) \int_{x-R}^{x+R} P(y) y dy x dx. \quad (7)$$

The formulas for U_{cc} and U_{nc} are valid for any atoms in liquids and gazes at sufficiently low temperatures. Concrete expressions for $P(r)$ have to be used in (5) and (7) to obtain the final formula. In particular, for ^4He , both electrons are at the state with $n = 1$, $l = 0$ (para–state). To obtain a simple formula for using in preliminary computations, we may ignore the electron–electron interactions in the cloud. Then the wave function of the electrons in the ^4He ground state is

$$\Phi(r_3, r_4) = \Psi(r_3) \Psi(r_4) \chi_p,$$

where r_3, r_4 are the electron coordinates,

$$\Psi(r) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}, \quad a = \frac{\hbar^2}{Ze^2 m}, \quad \chi_p = \frac{1}{\sqrt{2}} [|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle],$$

χ_p is antisymmetric spin wave function of the para–state.

The product $\Psi(r_3) \Psi(r_4)$ describes the symmetric radial part of the ground–state wave function. $|\Phi(r_3, r_4)|^2$ is the probability density to find one electron at the point r_3 , and another at the point r_4 . Because $|\chi_p|^2 = 1$, the probability density is

$$|\Phi(r_3, r_4)|^2 = \Psi^2(r_3) \Psi^2(r_4).$$

The charge density created by the two-electron cloud at the point r is

$$qP(r) = e|\Psi(r)|^2 + e|\Psi(r)|^2 = q|\Psi(r)|^2.$$

Using this formula and (5), (7), we obtain the expressions for U_{nc} and U_{cc} :

$$U_{nc} = -\frac{q^2}{R} + q^2 \left(\frac{1}{R} + \frac{1}{a} \right) e^{-2R/a}. \quad (8)$$

$$U_{cc} = \frac{q^2}{R} - q^2 \left(\frac{1}{R} + \frac{1}{a} \right) e^{-2R/a} - \frac{3q^2}{8a} e^{-2R/a} - \frac{q^2 R}{a^2} \left(\frac{R}{6a} + \frac{3}{4} \right) e^{-2R/a}. \quad (9)$$

Thus, the interaction potential between two atoms at a distance R is

$$U(R) = U_{nn} + U_{nc} + U_{nc} + U_{cc} = \frac{q^2}{a} \left[-\frac{1}{6} \left(\frac{R}{a} \right)^2 - \frac{3}{4} \left(\frac{R}{a} \right) + \frac{5}{8} + \left(\frac{a}{R} \right) \right] e^{-2R/a}. \quad (10)$$

It is obvious, that

$$U(R) \simeq -\frac{q^2 R^2}{a^3} e^{-2R/a}, \quad \text{as } R \gg a.$$

The exponential decrease of our potential U contrasts with R^{-6} -decrease in other formulas for ^4He - ^4He potential. The slow R^{-6} -decrease is provided by the use only the dipole interaction is taken into account in these formulas.

Our formula (10) for $U(R)$ does not contain arbitrary parameters. It is approximate, however, because we neglected the electron-electron interaction for obtaining $\Psi(r_3, r_4)$. Nevertheless, formula suggest an idea, that the semi-phenomenological potential of the form

$$U(R) = \left[A \left(\frac{R}{a} \right)^2 + B \left(\frac{R}{a} \right) + C + D \left(\frac{a}{R} \right) \right] e^{-\gamma R/a} \quad (11)$$

is of interest for the theory of the liquid ^4He maxon-roton spectrum, that considerably depends on the form of interatomic potential [7].

To take the electron interaction in the cloud into account, we have to use some realistic wave functions of the ^4He electrons in the ground state (see, e. g., [8]). For instance, the wave function of Hylleraas with three parameters gives additional terms up to R^6 inside the square brackets in (11). We emphasize that our formulas are designed for describing the two-atom interactions in the liquids and gases and we suppose, that no polarization effect exists for any pair of atoms in liquid due to its compensation.

The interaction potential of two atom in the vacuum in general has a contribution caused by the atom polarization. The atom polarization results in that the centers of electron clouds do not coincide with the nuclei and the clouds are deformed. The first estimate of a polarization effect can be easily described by our formulas with R in U_{nc} less than R in U_{nn} and U_{cc} . In such case, taking Δ as a shift of a positive and negative charge centers, we have a Buckingham-type formula

$$U(R) = U_{nn}(R) + 2U_{nc}(R - \Delta) + U_{cc}(R) = -\frac{2q^2 \Delta}{R(R - \Delta)} + V(R), \quad (12)$$

where $V(R)$ decreases as $\exp(-2R/a)$ as $R \gg a$. It is important, that Δ depends on R and $\Delta \rightarrow 0$ as $(R/a) \rightarrow \infty$. In other words, the dipole moment caused by the atom

polarization decreases as $(R/a) \rightarrow \infty$. It is very difficult to specify the dipole moment dependence on R . Nevertheless, we can say that R^{-6} -term in the L-J-potential is not correct in liquid media. As to the pair of ^4He atoms in vacuum, R^{-6} term is not correct due to the dependence $\Delta(R)$ (that is unknown unfortunately), and all of these properties are inherent for ^4He as the most compact inert gas.

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